Modeling Geochemical Reactive Transport of Concentrated Aqueous Solutions in Variably Saturated Media

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RESEARCH OBJECTIVE

Concentrated aqueous solutions (CAS) occur in many natural and contaminated environments, such as in the leakage of highly concentrated $NaNO_3$ electrolytes stored at DOE's Hanford site. They are generally considered as solutions with ionic strength larger than 1 M and can be more than 10 M. The main objectives in this paper are (1) to develop a model that can simulate the coupled geochemical and transport processes of CAS by developing a Pitzer ion–interaction module and incorporating it into a previously developed computer code, BIO-CORE$^{2D©}$, (2) to verify the developed module and the implementation into BIO-CORE$^{2D©}$, and (3) to validate the developed model through simulating laboratory experiments.

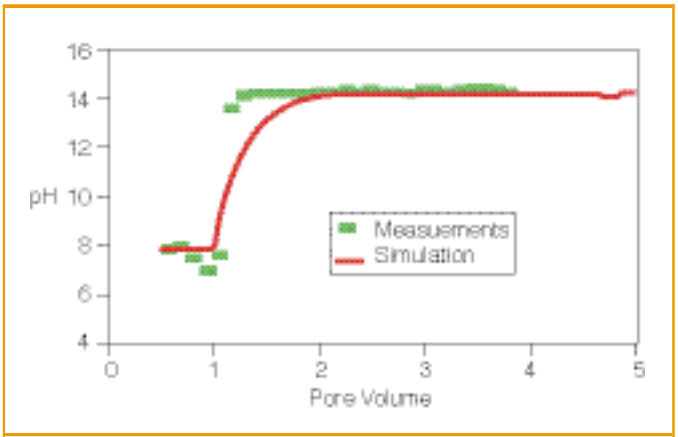

Figure.1. Simulated pH and measured pH of the effluent fluid during the injection of a highly alkaline-saline solution into a column filled with unsaturated sediments from the Hanford Site

APPROACH

The Pitzer ion-interaction model is considered the best representation of the ionic activity within CAS. In this study, a module of the Pitzer ion-interaction model is developed and implemented in a previously existing geochemical and microbiological reactive transport computer code, BIO-CORE$^{2D©}$ (Zhang, 2001). This code solves saturated-unsaturated flow, heat transfer, and solute transport coupled with chemical and microbial processes. A database storing Pitzer ion-interaction parameters was also developed. All parameters are temperature-dependent.

ACCOMPLISHMENTS

Several reported cases in the literature are used to verify the implementation of the Pitzer model. One of them calculates the activity coefficient of hydrochloric acid in a concentrated HCl-NaCl-KCl-H_2O system (298.15 K), at ionic strengths of 4, 5, 6, and 7 mol/kg, respectively, as a function of KCl concentration. We compared model results to the experimental data. Another case reports calculation of the activity coefficient of NaCl in a concentrated aqueous NaCl-Na_2SO_4-H_2O system—at ionic strengths of 2, 3, 4, and 6; and at 298.15 K and 318.15 K, respectively, as a function of Na_2SO_4 concentration. The results show that the activity coefficients calculated by BIO-CORE$^{2D©}$ are fairly close to the measurements. Wan et al. (2002) carried out a column experiment to understand the chemical interactions taking place in sediments from the Hanford Site during leakage of highly alkaline-saline solutions. In this experiment, highly alkaline-saline solution was injected into a column filled with unsaturated sediments from the Hanford Site. The experiment was modeled using BIO-CORE$^{2D©}$, and the results match the measured chemical composition of the effluent water. Figure 1 shows that the simulated pH matches the measured pH well. This result helps to improve our understanding of mineral precipitation and cation exchange processes during leakage of the tank waste solutions into sediments.

SIGNIFICANCE OF FINDING

The Pitzer phenomenological theory, as a basis for calculating ionic activities in concentrated aqueous solutions, is adequate for modeling high–ionic–strength problems. The Pitzer–type model generally reproduces the observed concentration trends for the Hanford case in which highly alkaline-saline solutions have leaked into sediments. Discrepancies could be attributed to uncertainties in cation exchange coefficients, surface areas, kinetics, and other thermodynamic data used in the model, as well as measurement errors.

RELATED PUBLICATIONS

Wan, J., T.K. Tokunaga, and J.T. Larsen, 2002, Evolution of REDOX tank waste plumes in Hanford vadose zone: A conceptual model developed through reactive transport studies, 2002 (submitted).

Zhang, G., 2001, Nonisothermal hydrobiogeochemical models in porous media. Ph.D. dissertation, University of La Coruña, Spain.

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